(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44875 A2

(51) International Patent Classification[7]: G03F 7/26

(21) International Application Number: PCT/US00/41781

(22) International Filing Date: 31 October 2000 (31.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/464,380 15 December 1999 (15.12.1999) US

(71) Applicant: NANOGEN, INC. [US/US]; 10398 Pacific Center Drive, San Diego, CA 92121 (US).

(72) Inventors: EVANS, John; 14055 Tahiti Way, Marina del Ray, CA 90292 (US). HAVENS, John, R.; 5628 Lamas Street, San Diego, CA 92122 (US). HARVEY, Noel; 3211 US 70 West, Efland, NC 27243 (US). SMOLKO, Dan; 20555 Bee Valley Road, Jamul, CA 91935 (US).

(74) Agents: EAGLEMAN, Patrick, S. et al.; Lyon & Lyon LLP, 633 West Fifth Street, Suite 4700, Los Angeles, CA 90071-2066 (US).

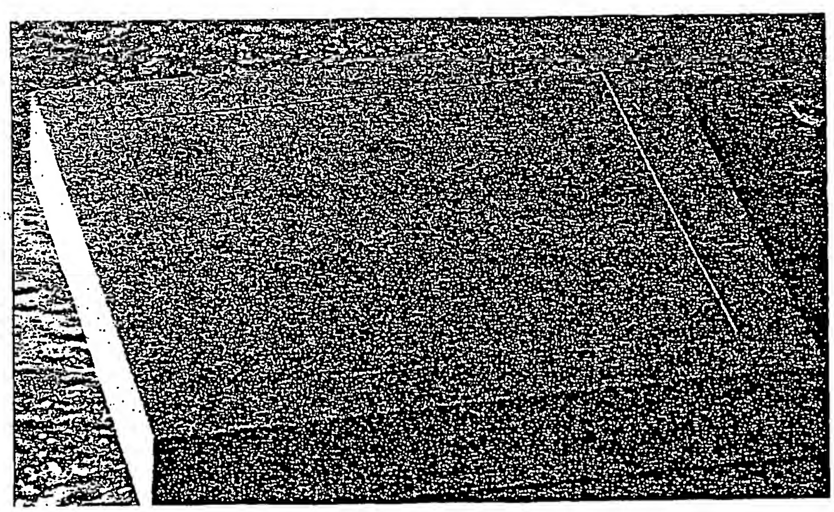
(81) Designated States (*national*): AU, BR, CA, CN, JP, KR, NZ.

(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
- *Without international search report and to be republished upon receipt of that report.*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MICROMOLDS FABRICATED USING MEMS TECHNOLOGY AND METHODS OF USE THEREFOR



(57) Abstract: A method of making microreaction molds for grafting and molding very thin films onto surfaces of materials such as microchips is provided. The methods utilize MEMS technology to achieve the manufacture of molds that have a high degree of consistency and uniformity in the thicknesses of the films applied to the surfaces. Use of MEMS technology allows such molds to be made with an accuracy of less than 1 μm in mold depth. The method provides for the manufacture of molds from a single transparent material that is able to be etched in a consistent manner. The method of this invention is particularly applicable to mass generation of microchip surfaces having uniform thin polymeric films bound thereto.

WO 01/44875 A2

MICROMOLDS FABRICATED USING MEMS TECHNOLOGY AND METHODS OF USE THEREFOR

FIELD OF THE INVENTION

The present invention relates to microscale systems and methods for making micromolds. More specifically, this invention relates to methods of making molds using MEMS (Micro Electro Mechanical Systems) technology for molding and grafting highly uniform materials in very thin layers onto the surface of electronically addressable microchips and other substrates.

BACKGROUND OF THE INVENTION

The following description provides a summary of information relevant to the present invention. It is not an admission that any of the information provided herein is prior art to the presently claimed invention, nor that any of the publications specifically or implicitly referenced are prior art to the invention.

The use of MEMS technology has been applied primarily to the electronics industry wherein a lithographic design environment is used that is significantly different from macrotooling techniques. Specifically, MEMS fabrication processes are subtractive in that typically, selected portions of material layered in a planar format by lithographic patterning (e.g., photoresist processes) are subtracted by various types of etching. Such processes are performed by layering material in a planar format typically on a very small scale on the order of between 0.2 μm and 10 mm with "out-of-plane" or vertical dimensions that are generally between 1 μm and 1 mm, usually between 1 μm and 500 μm.

Micromolding using MEMS technology has previously been applied to forming small structures such as described in U.S. Patents 5,735,985, and 5,919,364. Such mold systems are markedly different from that of the present invention. In still other microscale molding applications, some processes use pressurized molds where the mold is pressurized between 1 and 50 atm to prevent the formation of voids or volume shrinkage upon

polymerization of the molded materials. (Micro and Nano Patterning Polymers, Oxford University Press, 1993, ISBN 0841235813).

In contrast, we have developed a simple method using MEMS technology to make microreaction molds that can be used to generate directly on the surface of a substrate, such as a microchip, highly uniform films without complicated molding processes. Particularly, molds made by this method can be used to apply permeation layers to electronically addressable microchips in one step and in seconds thereby avoiding and eliminating latent manufacture problems previously associated with other types of processes for forming thin permeable films onto microchips. The molding apparatus and methods of this invention further ensure that the films are deposited only at the precise positions of the mold cavity with a highly uniform thickness.

Additionally, the mold product of this invention may be applied to attachment or grafting of multiple thin films or layers of a material onto a substrate in a manner that is applicable to high volume and inexpensive manufacture.

SUMMARY OF THE INVENTION

It is therefore a primary object of this invention to provide a method of making a micromold wherein said method uses applications of MEMS technology in a novel way. As used herein, MEMS technology means a fabrication process using primarily lithographic technologies such as those developed by the integrated circuit (IC) industry. Such technologies include lithography, dip coating, spin coating, sputtering, electro-plating, electroless-plating, evaporative deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition, thermal oxidation, wet chemical etching, vapor-phase etching, plasma etching, reactive-ion etching, deep reactive ion etching, ion milling and other microlayering and removal techniques. A fabrication process that uses such technologies allows for highly accurate and uniform deposition, lithographic patterning and controlled etching to selectively eliminate specific regions of underlying layers. MEMS technology further allows for accurate deposition of various types of layers in the

manufacturing process, such as metals and polymers. Structures produced by MEMS technology are inherently planar in that they usually have a vertical dimension generally less than about 1 mm and usually less than 500 μm. Moreover, such structures are relatively small, having areas generally on the order of less than 100 cm^2, usually less than 50 cm^2, ideally less than 10 cm^2.

In one aspect, the method provides for making micromolds in a material that is transparent to at least one wavelength of electromagnetic radiation. It is contemplated that materials useful for molds manufactured by the method of the invention provide for a highly uniform surface that can be micromachined or etched in such a manner that submicron uniformity can be realized with respect to the configuration of the mold cavity bottom surface. Materials contemplated include quartz, sapphire, geranium, silicon, fused silica (SiO2), polycarbonate, organic polymers, and polyacrylates. In a preferred embodiment, the electromagnetic wavelengths for which the materials are transparent include ultraviolet light (UV), visible light (Vis), and infrared (IR). Further, in some instances an upper surface of such materials is contemplated to possess a property of being opaque to the electromagnetic wavelength as described below.

In another aspect, the method of the invention contemplates the use of an anisotropic etching procedure as carried out in standard MEMS procedures. By anisotropic it is meant that material is removed from the surface area of the mold bottom being etched (i.e., the vertical etching) is subtracted at a much higher rate than lateral etching (i.e., the walls of the mold).

In another embodiment, as a result of highly refined milling or etching capability, the molds formed by the process provide for photolithographic molding of thin films to substrates, such films being applied consistently to within 0.5 μm thickness. These films may also be applied in any number of layers one upon the other.

In yet another embodiment, the method of the invention using MEMS technology is used to optionally apply opaque coatings to surfaces of the material other than that of the mold cavity. Manufacturing molds having opaque coatings applied to selective regions of

the mold provides for the ability to direct electromagnetic radiation exclusively through select areas of the mold devices, particularly the mold cavities, thereby providing a 'window' through which radiant energy is directed for activating materials being molded. In a preferred embodiment, such opaque coatings include metals and ceramics. Metals contemplated include chromium, titanium, tungsten, aluminum, silver, gold, platinum, and their oxides and nitrates.

In another aspect, the method provides for the simple manufacture of either singular or multiples of micromolds from a single block of material. The method further provides for the manufacture of multiple molds etched in a single block which further provides for inexpensive disposable molds and easy and affordable mass manufacture of thin films on substrate surfaces such as electronically addressable microchips. The mold cavities can be any size useful for molding thin films onto very small surface areas. In a preferred embodiment, the cavities can comprise areas generally between 1 μm^2 and 100 cm^2, usually between 1 μm^2 and 50 cm^2, preferable between 1 μm^2 and 10 cm^2 and having depths in the range of between 100 nm and 1 mm.

In still another aspect, the use of materials for constructing the molds that are transparent to at least one wavelength of electromagnetic radiation allows for the photoactivated polymerization of monomers used to form the thin layers directly in the molds. Such application is a novel application as it pertains to MEMS technology.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure **1** is an electron micrograph of a quartz mold having a mold cavity produced by MEMS techniques and not possessing an opaque coating. The mold depicted is designed as a single mold block.

Figures **2A** and **B** are schematic diagrams showing a sequence of a molding process wherein polymerizable monomer solution comprising a monomer and a polymerization initiator is applied to a mold cavity having an opaque coating on the sides and upper surface surrounding the mold cavity. After the monomer is applied, the microchip or other

surface to which a thin film is to be applied is brought into contact with the mold, and energy for polymerization is applied (e.g. an UV light source). Following polymerization, the surface with its and applied thin film can be removed from the mold.

Figures **3A-E** are a series of schematic diagrams showing examples of various mold shapes and dimensions having opaque coating applied thereto. Fig. **A** is a square mold in a square block; **B** is a circular mold in a circular block; **C** is a diamond shaped mold in a square block; **D** is a square mold in a circular block; and **E** is a pattern of a series of small circular molds in a circular block.

Figure **4** is a photograph showing an example of a mold looking through it from a perpendicular perspective. The light colored band encircling the mold comprises an opaque coating on the upper surface surrounding the mold cavity.

Figure **5** is a photograph showing a perspective view of a circular micromold such that it can be seen that the frame and sides of the mold are coated with an opaque material.

Figure **6** is a photomicrograph depicting an electronically addressable microchip wherein a thin film using a circular mold made by the method of the invention has been deposited onto the surface of the microchip.

Figure **7** is a bar graph showing the extraordinary consistency of thin films applied to a substrate surface using a mold made by the method of the invention.

Figure **8A-P** is a schematic showing a mold manufacture process using MEMS technologies. Detail **8H-P** depicts use of MEMS technology to optionally apply an opaque coating such as a metal.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, a method using MEMS technology is provided for the manufacture of high-precision micromolds of unibody construction. As used herein, MEMS technology means a fabrication process using primarily lithography technologies such as those developed by the integrated circuit (IC) industry. Such methods include lithography, dip coating, spin coating, sputtering, electro-plating, electroless-plating,

evaporative deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition, thermal oxidation, wet chemical etching, vapor-phase etching, plasma etching, reactive-ion etching, deep reactive ion etching, ion milling and other microlayering and removal techniques. This fabrication process allows for highly accurate and uniform deposition, lithographic patterning and controlled etching techniques to selectively eliminate underlying layers. MEMS technology further allows for accurate deposition of various types of layers in the manufacturing process, such as metals and polymers. Structures produced by MEMS technology are inherently planar in that they usually have a vertical dimension generally less than about 1 mm and usually less than about 500 μm and preferably less than about 100 μm. Moreover, such structures are relatively small, having areas generally less than 100 cm^2 and preferably less than 10 cm^2.

The method of the invention differs from other MEMS micromold manufacture systems in several ways. First, the materials out of which the molds are constructed are transparent to at least one wavelength of electromagnetic radiation. This transparency provides the ability to perform polymerization reactions of polymerizable monomers directly in the mold cavities for polymer formation and bonding to substrate surfaces. In a preferred embodiment, the radiant energy is channeled directly through the body of the mold material and into the mold cavity. In one embodiment, the mold material may include at least an upper surface that has a property of being opaque to said wavelength of radiation. In a preferred embodiment, such opaque property can be imparted to the material by the application of opaque coatings onto selected areas of the mold material to keep the radiant energy channeled exclusive into the mold cavity. Thus, in such embodiment, "windows" are provided through which polymerization initiating energy (e.g., UV, Vis, or IR radiation) can be directed for inducing the polymerization of solutions dispensed into the mold cavities.

The mold substrate materials further provide for highly accurate micromachining or etching capability such that accuracy of mold cavity depths can be precisely manufactured to within 0.5 μm.

The method of manufacturing such molds further provides for the ability to designed mold cavity shapes in any configuration. Examples of various configurations are provided in Figs. **3A-E**.

The manufacture of micromolds as described herein provides for molds which overcome problems experienced with other thin film deposition techniques. Specifically, thin films may be applied to surfaces with a much greater consistency of film thickness and area. For instance, use of spin-coating to apply thin films to electronically addressable microchips results in films that have a high degree of variability in thickness and area between individual chips. The high variability causes large variations in realized electronic potential between individual electronic pads of such microchips so that it is difficult to correlate data involving transported molecules from test solutions used in connection with microchips having such coatings. In contrast, molds made using MEMS technology provide for deposition of films that have a thickness between individual chips consistently within 0.5 μm across the entirety of the area to which the film is applied. Moreover, thin films may be molded in layers one upon the other in highly accurate fashion.

In an example of the manufacturing process, Figure **8A-P** depicts various steps that may be used to form the molds. In figure **8A**, a cross-section of a quartz wafer is depicted (1) having a front surface (2) and a back surface (3). As shown in **8B,** a layer of undoped polysilicon is deposited on the front (4) and the back (5) of the wafer using Low Pressure Chemical Vapor Deposition (LPCVD), as is commonly practiced in the art. This layer protects the wafer.

Next, a photoresist layer (6) is spun onto the front of the wafer and patterned (Fig. **8C**), leaving the front polysilicon layer (4) exposed in specified regions (7). As depicted in **8D**, any of a class of commonly used polysilicon plasma etch process is employed to remove the polysilicon in the specified regions (7), exposing the quartz in the regions (8), while leaving the backside polysilicon layer (5) intact. The photoresist layer (6) is then stripped (**8E**), exposing the now patterned polysilicon layer (5). The quartz wafer is then

treated with hydrofluoric acid to form wells (9) (Fig. **8F**). The polysilicon layers (4) and (5) are then removed using a wet KOH etch, leaving the shaped quartz wafer (1), now containing wells (9), and exposed faces (2) and (3), (Fig. **8G**).

The MEMS manufacturing process may optionally further be used to apply a metal layer (10), made of, for example, titanium, by sputtering onto the front side of the quartz wafer (1), as shown in Fig. **8H**. As before, a photoresist layer (11) is applied and patterned (**8I**), and then the wafer is etched using an wet etchant appropriate for the metal used, forming the open areas (12) (Fig. **8J**). The photoresist layer (11) is then stripped, leaving the structure as shown in Fig. **8K**, containing a quartz wafer (1), a patterned titanium layer (10), and recessed mold cavities (12).

As shown in Fig. **8L**, the wafer (1) can be cut into regions (13) forming individual mold die (14) or left whole as shown in Fig. **8K**. This cutting may be accomplished with a mechanical dicing saw, or may be accomplished using an ultrasonic cutting apparatus.

Next, in embodiments where the mold cavities have been separated into individual die, they may be stacked as shown in Fig. **8M** with another quartz wafer (15) so that the quartz die (14) is turned over such that its front surface (2) and patterned metal layer (10) face downward with the secondary wafer (15) protecting the bottom surface of the mold die.

When this stack is placed in a metal sputtering or evaporation system, only the sides (17) of the quartz die are exposed (Fig. **8N**). The quartz die (14) and quartz blank (15) are then separated as indicated Fig. **8O**.

This manufacturing method results in a micromold as indicated in Fig. **8P**. The quartz die (14) is completely coated with a metal layer along the sides (17), and coated with a patterned layer along the front face (2), but is not covered along the back face or 'window' (3), or in the mold cavity regions (9).

As will be clear to one skilled in the art, the foregoing description of the schematic shown in Fig. **8A-P** is provided for purposes of explanation only, and it will be apparent to such a skilled artisan that the specific details are not required in order to practice the

invention. For example, any number of mold substrate materials may be employed so long as they have a transparent quality allowing for transmission of select wavelengths of electromagnetic irradiation. Moreover, opaque materials other than titanium may be employed as described above. Additionally, any number of MEMS techniques may be used to apply and remove layers such as polysilicon, photoresist, and opaque coatings as used in other instances well-known in the electronics industry. Thus, the forgoing descriptions of specific embodiments of the present invention are presented for purposes of illustration and description. They are not intended to be exhaustive or to limit the invention to the precise forms disclosed. Many modifications and variations are possible in view of the above teachings.

Generally, application of the molds so manufactured are contemplated to be used in the formation of thin films onto substrate surfaces such as electronically addressable microchips. In a preferred embodiment substances used for film deposition include polymerizable monomers selected from the group consisting of acrylamide, bisacrylamide, methacrylamide, *N*-alkyl acrylamides, functionalized ethylene glycol derivatives, *N*-vinyl pyrrolidinone, bis-cystamine, acrylates, methacrylates, and acrylonitriles where alkyl refers to a carbon chain. Other monomers may be selected from the group consisting of epoxides, alkenyl moieties including, but not limited to, substituted or unsubstituted α, β unsaturated carbonyls wherein the double bond is directly attached to a carbon which is double bonded to an oxygen and single bonded to another oxygen, nitrogen, sulfur, halogen, or carbon; vinyl, wherein the double bond is singly bonded to an oxygen, nitrogen, halogen, phosphorus or sulfur; allyl, wherein the double bond is singly bonded to a carbon which is bonded to an oxygen, nitrogen, halogen, phosphorus or sulfur; homoallyl, wherein the double bond is singly bonded to a carbon which is singly bonded to another carbon which is then singly bonded to an oxygen, nitrogen, halogen, phosphorus or sulfur; and alkynyl moieties wherein a triple bond exists between two carbon atoms.

Since such monomers must be induced to polymerize using for example UV irradiation directed through the mold 'window', representative classes and examples of UV

photoinitiators which may be used include benzyl ketal photoinitiators such as 2,2-dimethoxy-2-phenylacetophenone, benzoin ethers such as 2-methoxy-2-phenylacetophenone, hydroxy alkyl phenyl ketones such as 2-hydroxy 2-methyl-1-phenyl-propan-1-one, dialkoxy acetophenones such as 2,2-diethoxy acetophenone, benzoyl cyclohexanol ketones such as 1-hydroxycyclohexyl phenyl ketone, benzoyl phosphine oxides such as 2,4,6-trimethylbenzoyl diphenylphosphine oxide, alkylthiophenyl morpholino ketones such as 1-methyl-1-(4-methylthiophenyl)-2-morpholino propan-1-one, morpholinophenyl amino ketones such as 2-benzyl-2-N,N-dimethylamino-1-(4-morpholinophenyl)-1-butanone. Additional UV photoinitiator classes which work in the presence of hydrogen or electron donors (coinitiators) include phenones such as benzophenone, thioxanthones such as chlorothioxanthone, quinones such as camphorquinone, and ketocoumarins such as 1-phenylketocoumarin and the benzil class.

Where polymerization initiation is to be carried out using thermal energy in the form of IR irradiation, the monomer solution and mold are heated to a specific temperature range thereby causing activation of heat sensitive polymerization initiators such as azobisisobutyronitrile (AIBN). In such embodiment, the mold cavity may be maintained at a temperature of between 15 and 250°C for a time sufficient for film molding.

Representative chemical and thermal initiators include azonitriles such as 2,2'-azobisisobutyronitrile, azo derivatives such as 2,2'-azobisisobutyramidine, alkylperoxides such as tert-butyl peroxide, acyl peroxides such as benzoyl peroxide, hydroperoxides such as tert-butyl hydroperoxide and ketone peroxides such as acetone cyclic diperoxide, persulfate initiators such as ammonium and potassium persulfate, and azide initiators such as *p*- toluenesulfonyl azide. Some of these, such as ammonium persulfate (APS), work in the presence of coinitiators such as tetramethylethylene diamine (TEMED).

In a most preferred embodiment, initiators may be selected from the group consisting of azobisisobutyronitrile (AIBN), ammonium persulfate and tetramethylethylenenediamine (APS/TEMED), benzol peroxide, and a solution of 50%

2,4,6-trimethylbenzoyl diphenylphosphine oxide and 50% 2-hydroxy 2-methyl-1-phenyl-propan-1-one (D4265).

Formation of the thin films on a substrate surface such as a microchip using the molds made by the method of the invention may be accomplished, for example, by the following procedure.

Step 1. The microchip surface is cleaned and treated with a covalent coupling agent to obtain preferential surface adhesion. Since it is desired for the polymeric material being formed in the mold to adhere to the surface of a substrate, e.g. an electronically addressable microchip, in a preferred embodiment, the surface to which the thin film is to be applied is used to form the 'top' of the mold and may be precoated with a covalent coupling agent such as those commercially available and well known to those skilled in the art. For example, methacryloxypropyl trimethoxysilane may be applied to the substrate surface allowing chemical moieties of the permeation layer polymer matrix to bond to the substrate.

Step 2. The mold cavity is precleaned with acetone, ethanol, and water prior to the addition of the monomer solution. Additionally, the mold cavity is treated with a mold-form release agent. In a preferred embodiment, perfluorochlorosilane (Gelest S1H5841.0) can be deposited by vapor deposition in a vacuum for 15 minutes. Other useful release agents include chlorosilane and alkoxysilane. This is then rinsed with a stream of ethanol followed by water and dried for 1 hour at 100°C. An alternative method of treating the molds may include plasma enhanced chemical vapor deposition (PECVD) deposition of fluorine on the mold cavity surface as is well known in the art.

Step 3. The polymerizable monomer/initiator solution is deposited onto the surface of the mold. (The mold may be oriented in either a right-side up or an upside-down position. Where the mold is below facing up, the solution may be deposited into the mold well. Where the mold is above facing down, the solution may be deposited onto the surface of the microchip.)

Step 4. The material onto which a thin film is to be applied, such as a microchip, forms the 'top' of the mold, and is brought into contact with the mold such that it abuts the frame surrounding the mold cavity. The monomer/initiator solution is induced to polymerize or 'cure' by contacting the solution with an initiator activator source. Such source is preferably UV irradiation that is channeled or shined through the transparent window. In a preferred embodiment, this source is channeled or uniformly distributed through the window for generally between 2 and 2000 seconds, usually between 2 and 300 seconds, and preferably between 2 and 30 seconds.

Generally, where UV irradiation is used, the light energy is contemplated to comprise an energy range of between 0.1 milliWatt/cm^2 and 1000 milliWatt/cm^2. Preferably, the UV intensity is 100 mW/cm^2 using 320-390 nm wavelengths.

Step 5. Following polymerization in step 4, the microchip with its adherent thin film is separated from the mold cavity and washed with distilled water.

Step 6. The thin film coated microchips are then aspirated to remove extraneous reactants then dried.

Step 7. The mold is immediately available for use in another molding reaction wherein steps 1-6 may be repeated.

As is understandable to one of skill in the art, the molding apparatus and method is amenable to automation. Multiples of molds may be constructed in an assembly line process for mass production of substrates having highly uniform thin film coatings applied thereto.

Modifications and other embodiments of the invention will be apparent to those skilled in the art to which this invention relates having the benefit of the foregoing teachings, descriptions, and associated drawings. The present invention is therefore not to be limited to the specific embodiments disclosed but is to include modifications and other embodiments which are within the scope of the appended claims. All references are herein incorporated by reference.

We Claim:

1. A method of making a microreaction mold comprising:

   in a material transparent to at least one wavelength of electromagnetic radiation, said material having an upper surface, a lower surface, and one or more side surfaces, forming into said upper surface at least one mold cavities by a MEMS technology process.

2. A method of making a microreaction mold according to claim 1 wherein said method includes microlayering and removal process step techniques selected from the group consisting of lithography, dip coating, spin coating, sputtering, electro-plating, electroless-plating, evaporative deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition, thermal oxidation, wet chemical etching, vapor-phase etching, plasma etching, reactive-ion etching, deep reactive ion etching, and ion milling.

3. A method of making a microreaction mold according to claim 1 wherein said material comprises a material selected from the group consisting of an inorganic glass, fused silica, silicon dioxide, transparent crystalline, quartz, sapphire, geranium, silicon, organic polymers, polyacrylates, and polycarbonates.

4. A method of making a microreaction mold according to claim 1 wherein part or all of said upper surface excluding said mold cavities have a property of being opaque to said wavelength of electromagnetic radiation.

5. A method of making a microreaction mold according to claim 4 wherein said opaque property is provided by the application of an opaque coating to all or part of said upper surface excluding said mold cavities, said application provided using

microlayering and removal process step techniques selected from the group consisting of lithography, dip coating, spin coating, sputtering, electro-plating, electroless-plating, evaporative deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition, thermal oxidation, wet chemical etching, vapor-phase etching, plasma etching, reactive-ion etching, deep reactive ion etching, and ion milling.

6. A method of making a microreaction mold according to claim 5 wherein said opaque coating comprises a material selected from the group consisting of a plastic, a ceramic, a metal, chromium, titanium, tungsten, aluminum, gold, silver, platinum, metal oxides, and metal nitrides.

7. A method of making a microreaction mold according to claim 1 wherein and said material comprises a material transparent to ultraviolet light radiation.

8. A method of making a microreaction mold according to claim 1 wherein at least one of said mold cavities has area dimensions of between 1 μm^2 and 100 cm^2.

9. A method of making a microreaction mold according to claim 1 wherein at least one of said mold cavities has a depth of between 100 nm and 1 mm.

10. A method of making a microreaction mold according to claim 1 wherein at least one of said mold cavities has a planar bottom.

11. A method of making a microreaction mold according to claim 1 wherein at least one of said cavities has applied thereto a coating that is not opaque to said wavelength of electromagnetic radiation.

12. A method of making a microreaction mold according to claim 11 wherein said coating is selected from the group consisting of perfluorochlorosilane, chlorosilane, and alkoxysilane.

13. A method of making a microreaction mold according to claim 1 wherein a single block of material has a plurality of mold cavities.

14. A method of making a microreaction mold according to claim 1 wherein a single block of material has one mold cavity.

15. A method of making a microreaction mold according to claim 1 wherein all or part of said side surfaces have the property of being opaque to said wavelength of electromagnetic radiation.

16. A method of making a microreaction mold according to claim 15 wherein said opaque property is achieved by coating all or part of said side surfaces with a coating material.

17. A method of making a microreaction mold according to claim 16 wherein said coating material comprises a material selected from the group consisting of a plastic, a ceramic, a metal, chromium, titanium, tungsten, aluminum, gold, silver, platinum, metal oxides, and metal nitrides.

18. A microreaction mold made by the method of claim 1 comprising:

a material transparent for at least one wavelength of electromagnetic radiation, said material having an upper surface, a lower surface, and one or more side surfaces, said upper surface having incorporated therein at least one mold cavity.

19. A microreaction mold according to claim 18 wherein said material comprises a material selected from the group consisting of an inorganic glass, fused silica, silicon dioxide, transparent crystalline, quartz, sapphire, geranium, silicon, organic polymers, polyacrylates, and polycarbonates.

20. A microreaction mold according to claim 18 wherein and said transparent material comprises a material transparent to ultraviolet light radiation.

21. A microreaction mold according to claim 18 wherein part or all of said upper surface excluding said cavitites has the property of being opaque to said wavelength of electromagnetic radiation.

22. A microreaction mold according to claim 21 wherein said opaque property is provided by the application of an opaque coating to all or part of said upper surface excluding said mold cavities, said application provided using process steps selected from the group consisting of lithography, dip coating, spin coating, sputtering, electro-plating, electroless-plating, evaporative deposition, chemical vapor deposition, plasma enhanced chemical vapor deposition, thermal oxidation, wet chemical etching, vapor-phase etching, plasma etching, reactive-ion etching, deep reactive ion etching, ion milling and microlayering and removal techniques.

23. A microreaction mold according to claim 22 wherein said optional opaque coating comprises a material selected from the group consisting of a plastic, a ceramic, a metal, chromium, titanium, tungsten, aluminum, gold, silver, platinum, metal oxides, and metal nitrides.

24. A microreaction mold according to claim 18 wherein said at least one mold cavities has area dimensions of between 1 μm^2 and 100 cm^2.

25. A microreaction mold according to claim 18 wherein at least one of said mold cavities has a depth of between 100 nm and 1 mm.

26. A microreaction mold according to claim 18 wherein said at least one mold cavities has a planar bottom.

27. A microreaction mold according to claim 18 wherein at least one of said cavities has applied thereto a coating that is not opaque to said wavelength of electromagnetic radiation.

28. A microreaction mold according to claim 27 wherein said nonopaque coating is selected from the group consisting of perfluorochlorosilane, chlorosilane, and alkoxysilane.

29. A microreaction mold according to claim 18 wherein a single block of material has a plurality of mold cavities.

30. A microreaction mold according to claim 18 wherein a single block of material has a one mold cavity.

31. A microreaction mold according to claim 18 wherein all or part of said side surfaces are coated with a coating material that renders all or part of said side surfaces opaque to said wavelength of electromagnetic radiation.

32. A microreaction mold according to claim 18 wherein one or more side surfaces is coated with a coating material that is opaque to said wavelength of electromagnetic radiation.

33. A microreaction mold according to claim 32 wherein said coating material comprises a material selected from the group consisting of a plastic, a ceramic, a metal, chromium, titanium, tungsten, aluminum, gold, silver, platinum, metal oxides, and metal nitrides.

34. A method of using a microreaction mold of claim 18 to mold a film onto a substrate surface comprising:

a. dispensing onto either of said mold or said said substrate surface a solution;

b. bringing into contact said substrate surface with said mold;

c. directing through said mold electromagnetic radiation, said radiation having a wavelength and energy sufficient to initiate polymerization of said solution; and

d. separating said mold from said substrate to reveal said film molded to said substrate surface.

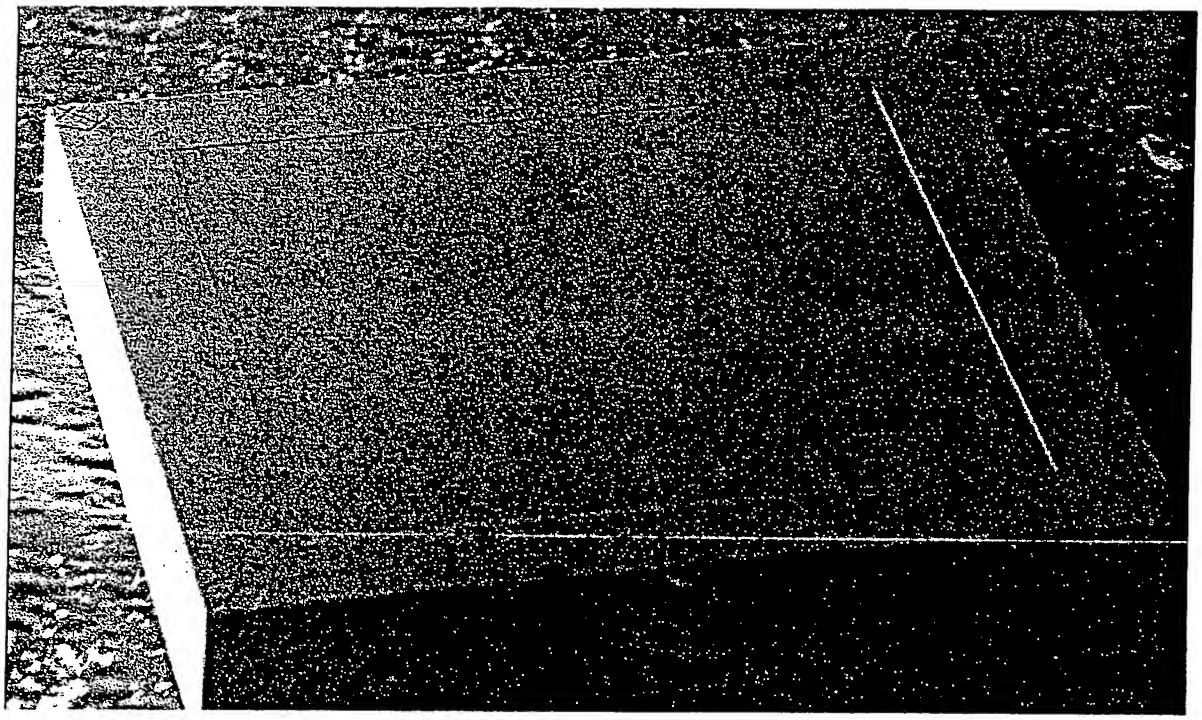


Fig. 1

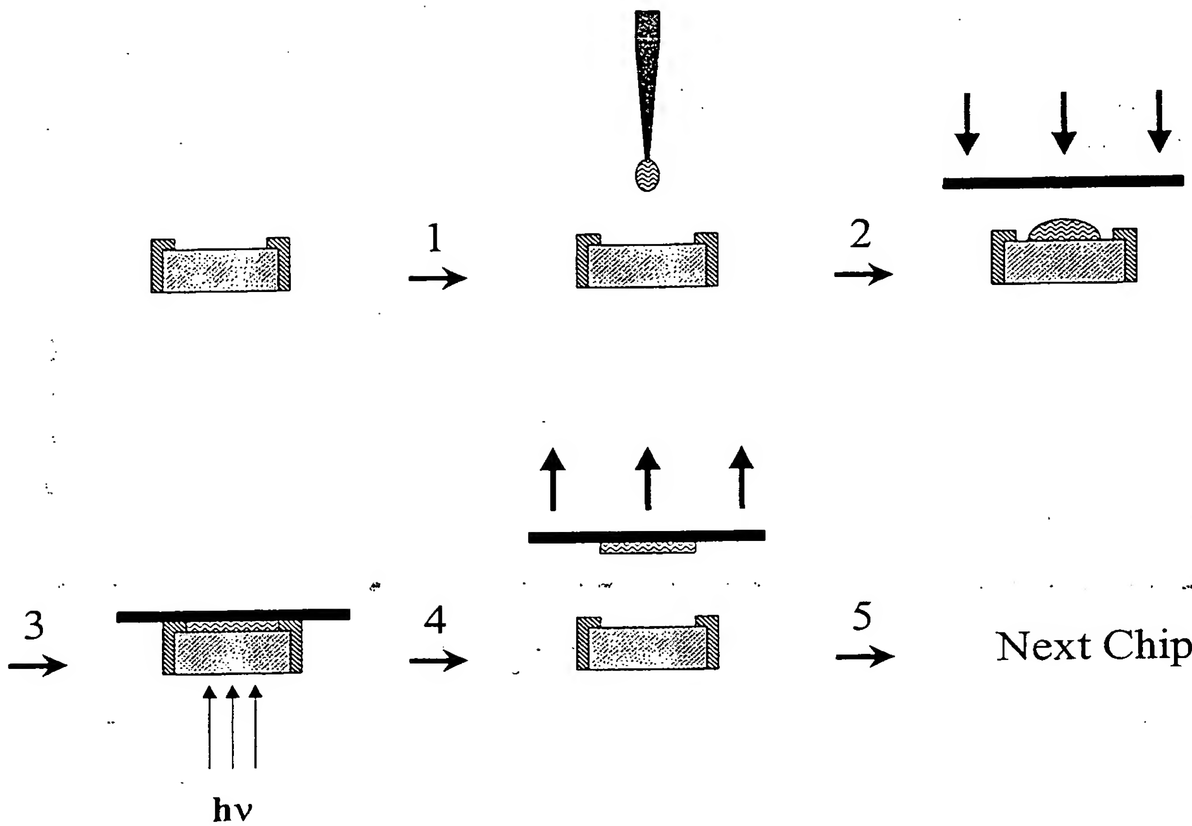


Fig. 2A

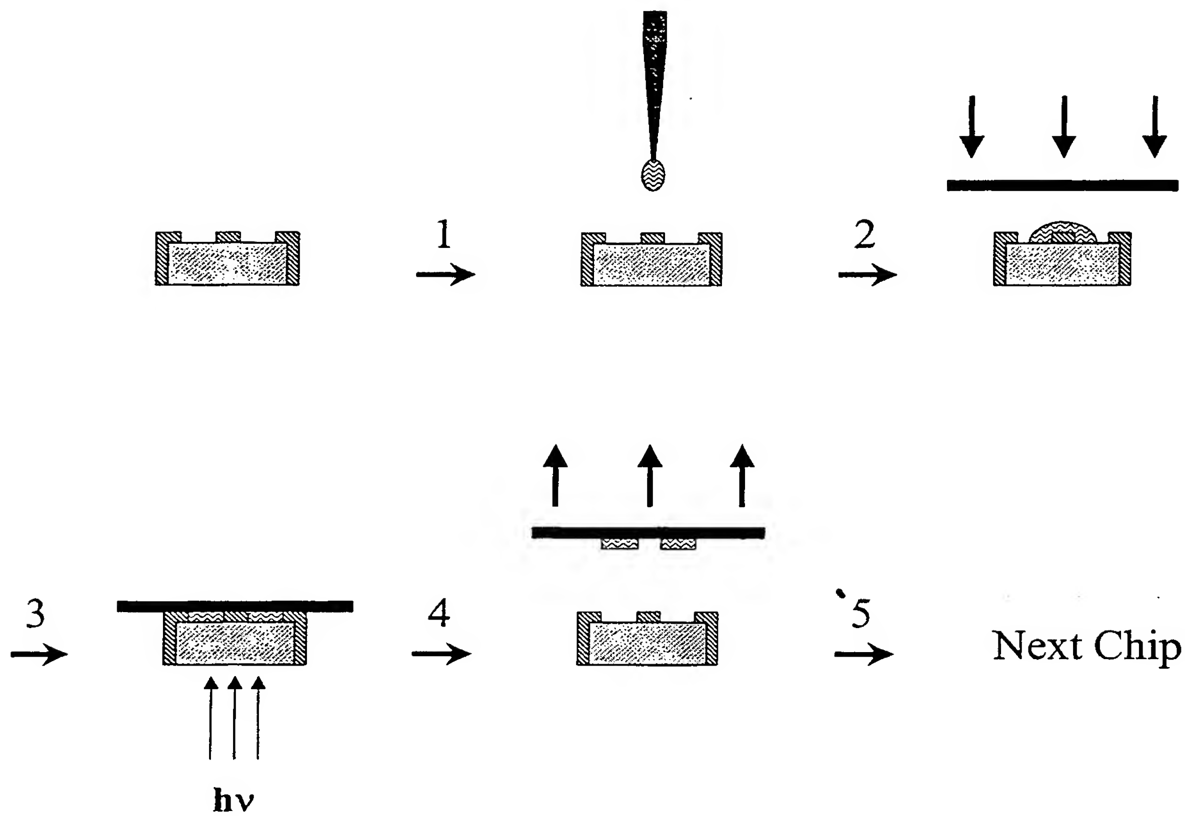


Fig. 2B

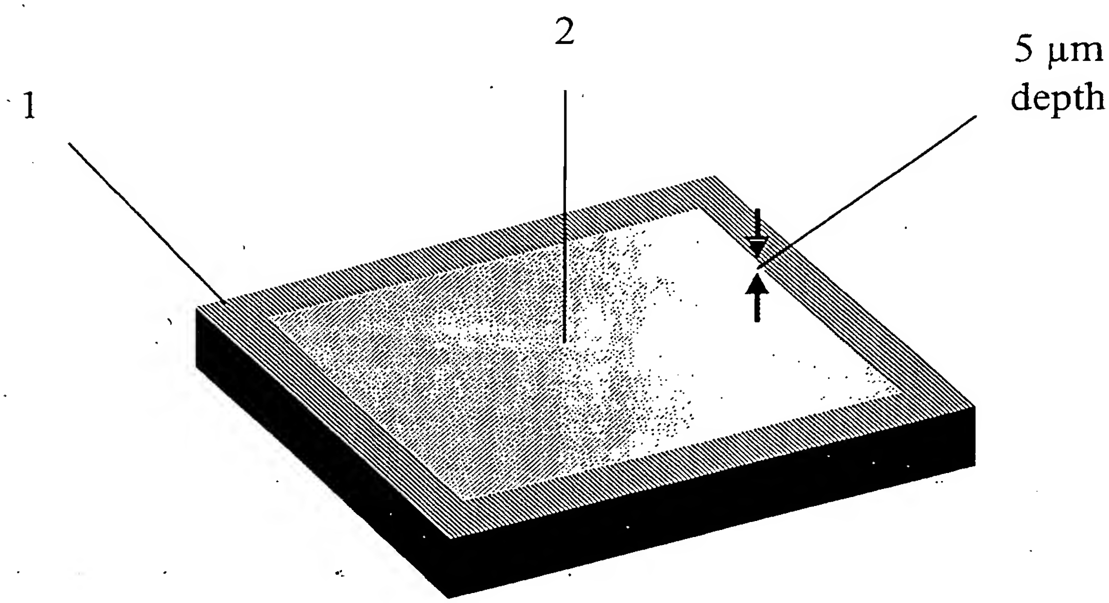


Fig. 3A

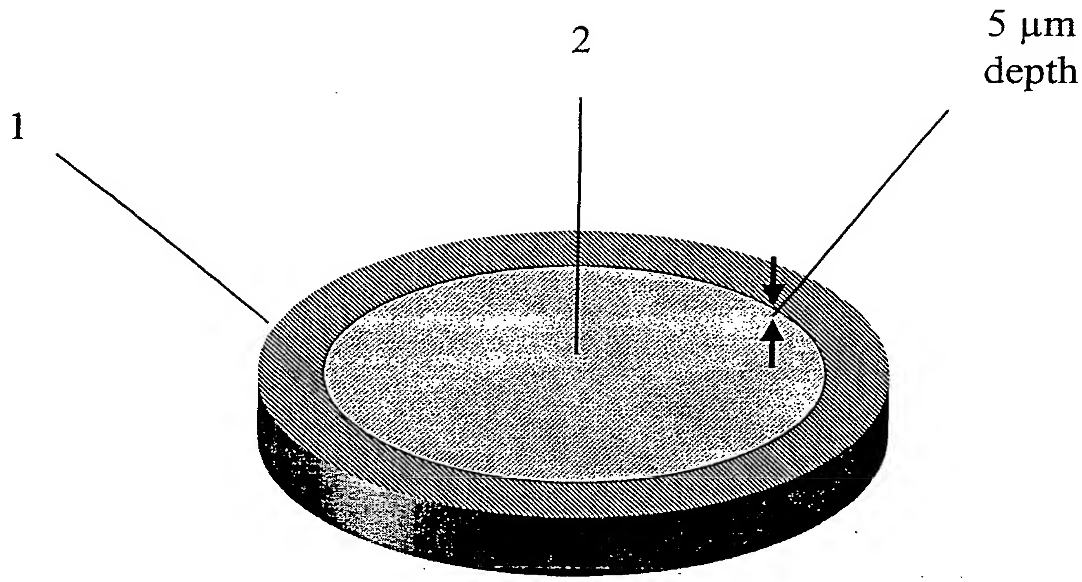


Fig. 3B

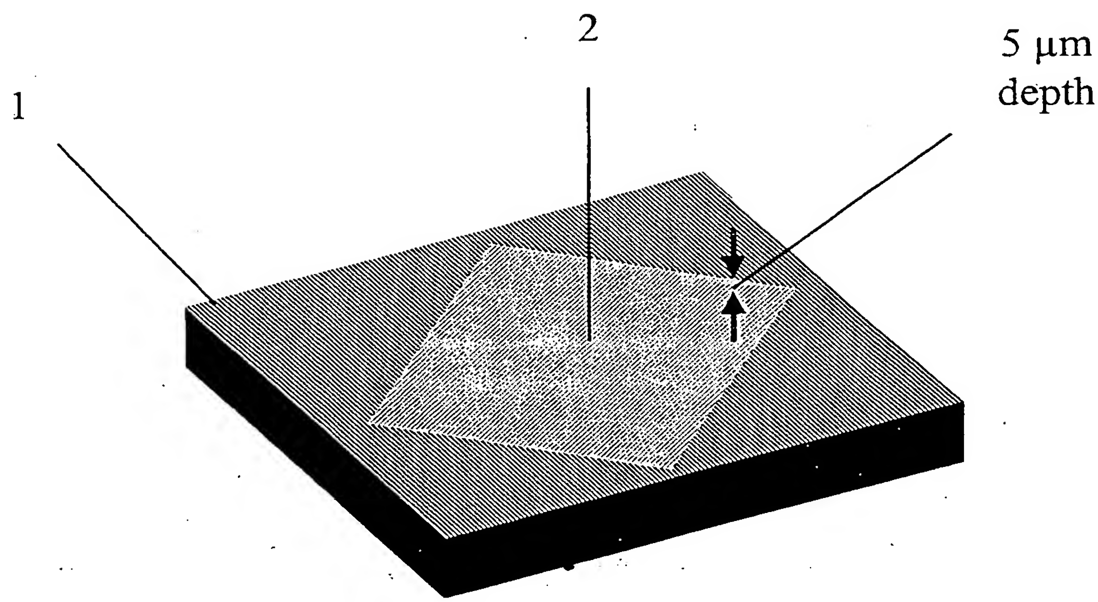


Fig. 3C

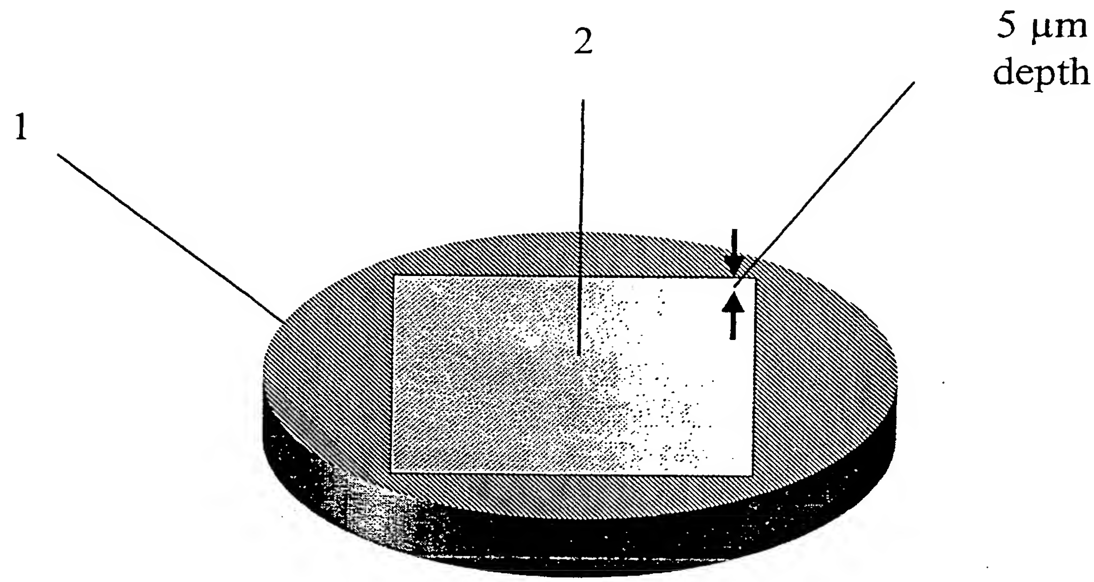


Fig. 3D

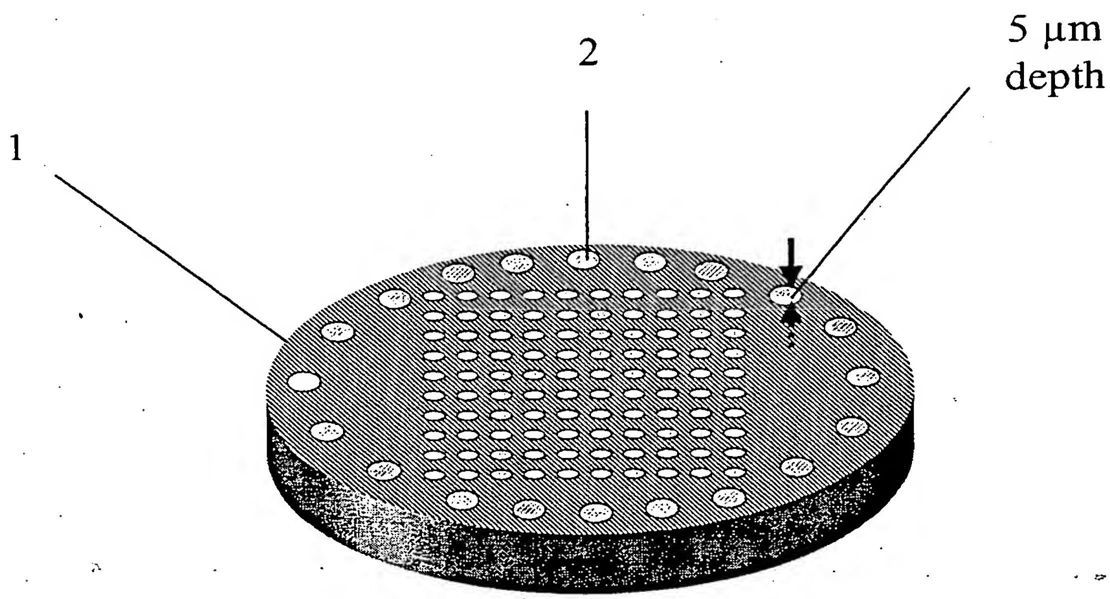


Fig. 3E

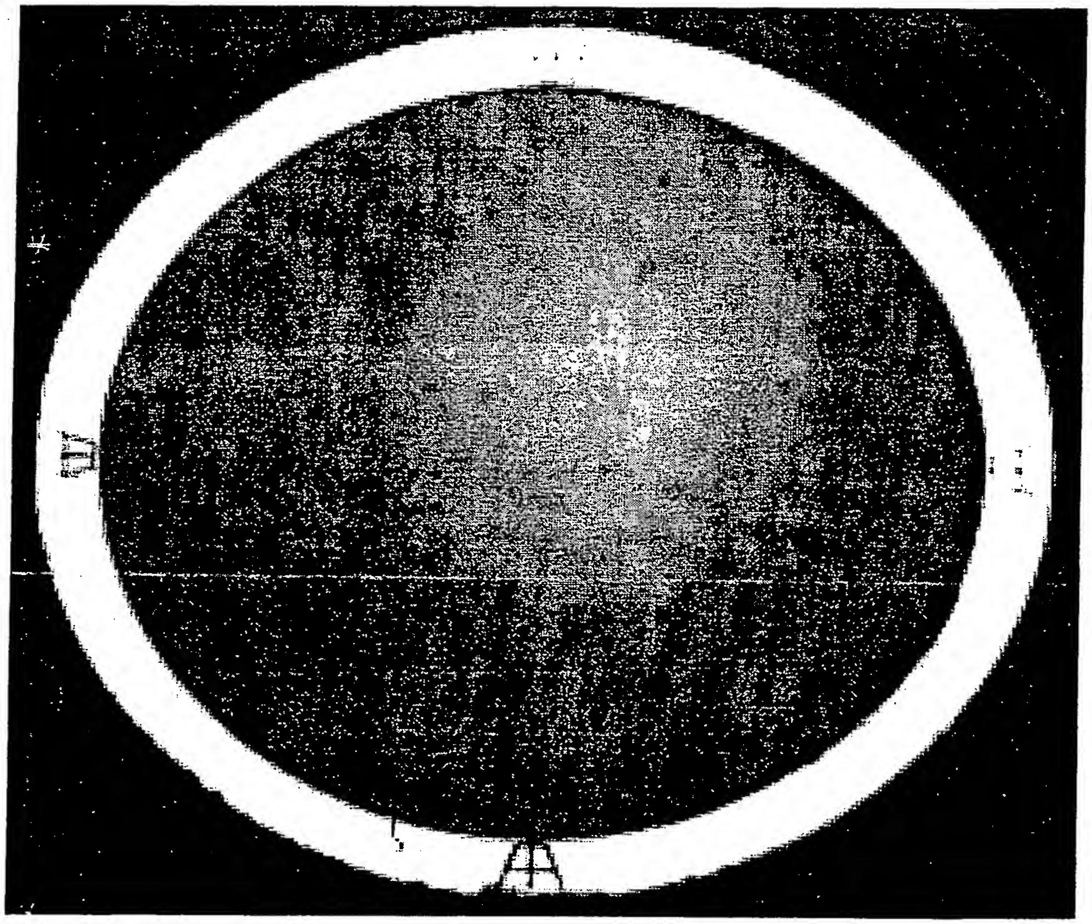


Fig. 4

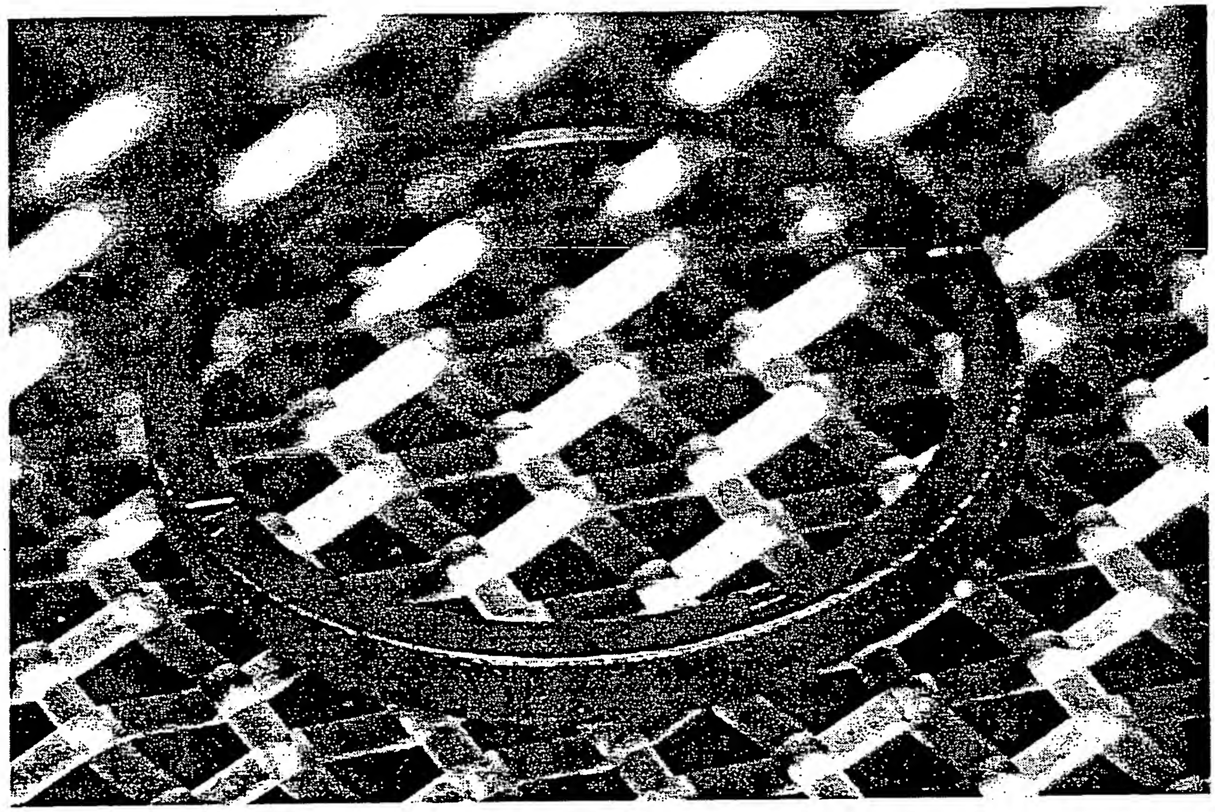


Fig. 5

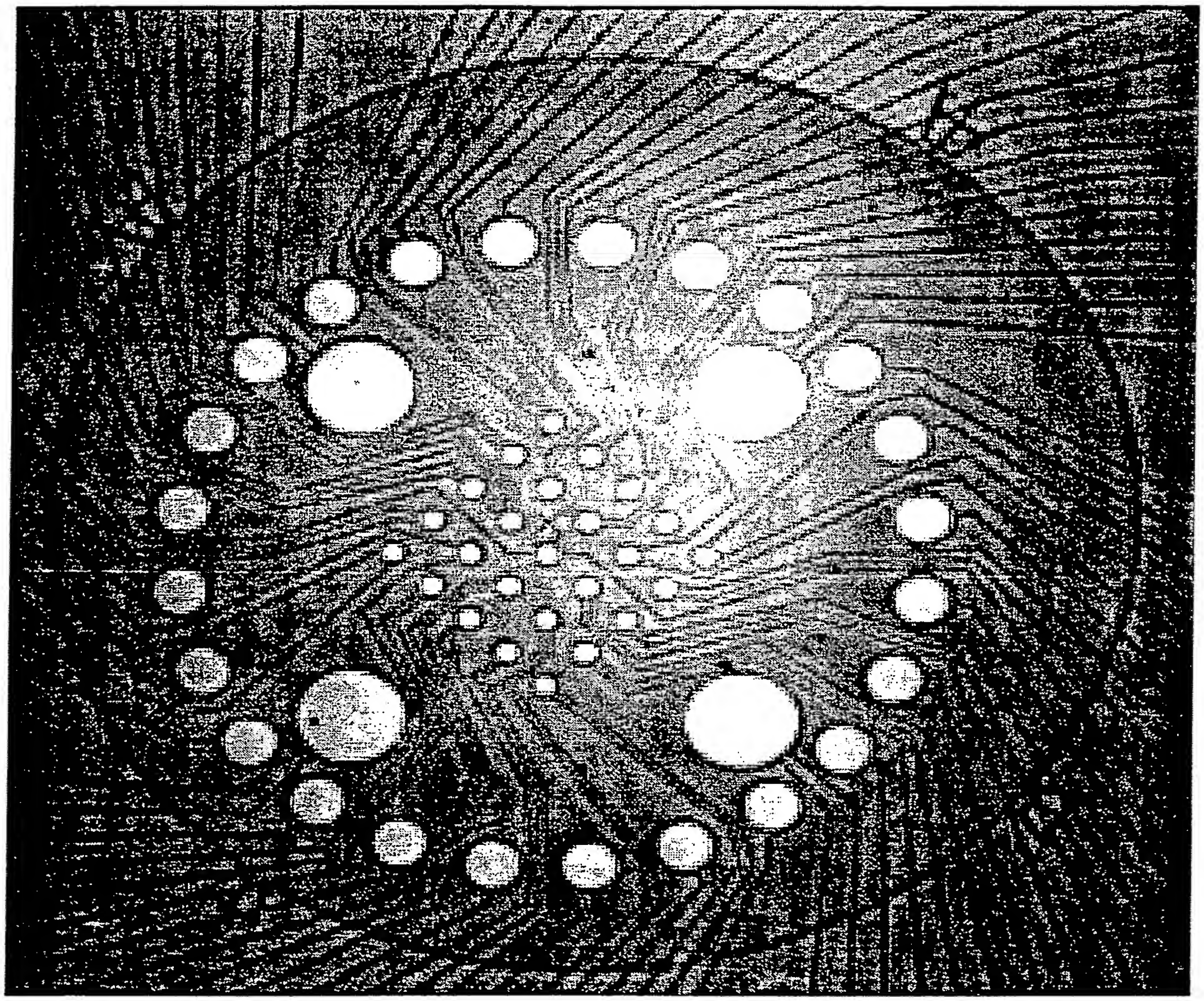


Fig. 6

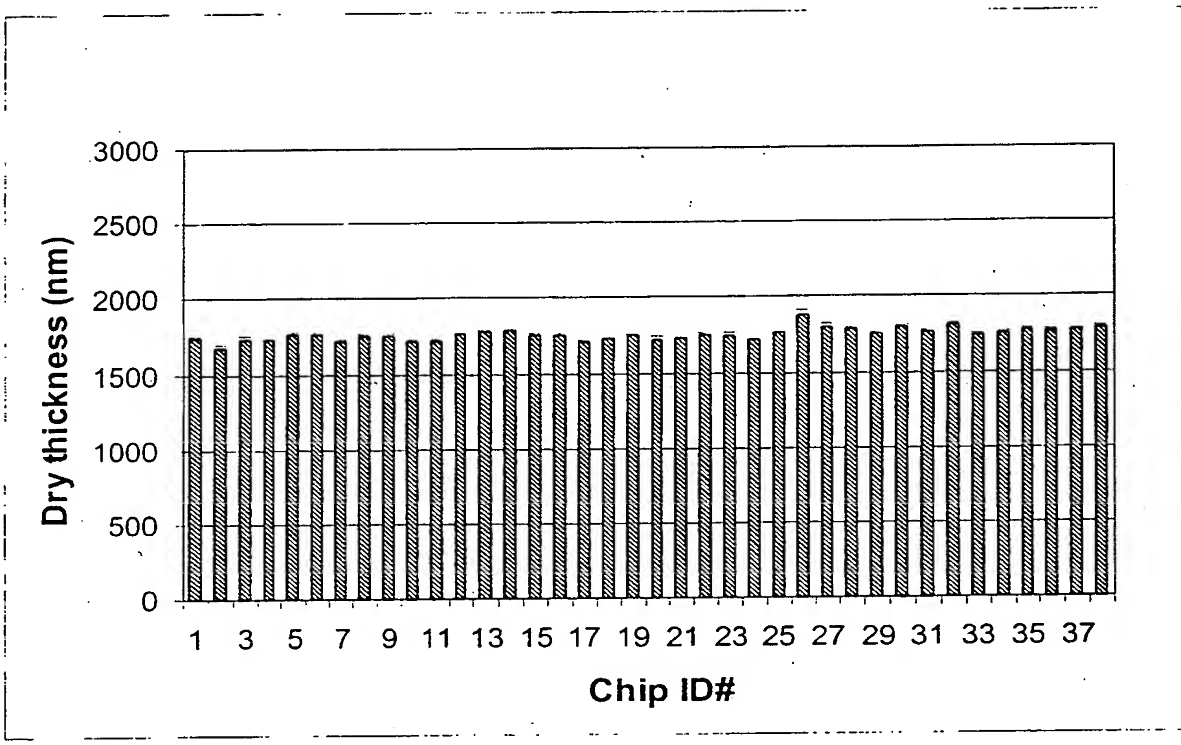

3000
2500
2000
1500
1000
500
0
Dry thickness (nm)
1 3 5 7 9 11 13 15 17 19 21 23 25 27 29 31 33 35 37
Chip ID#

Fig. 7

Fig. 8A

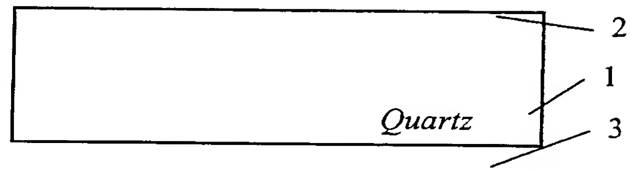


Fig. 8B

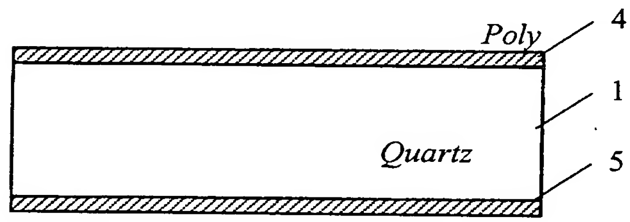


Fig. 8C

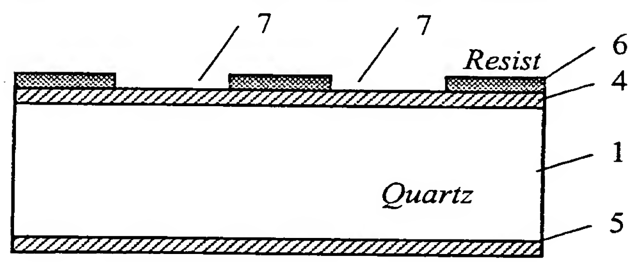


Fig. 8D

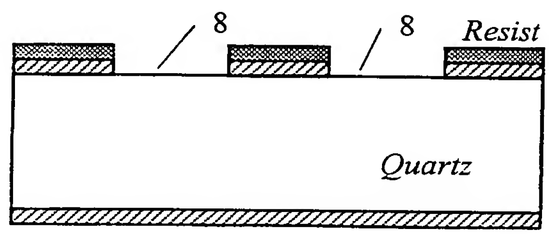


Fig. 8E

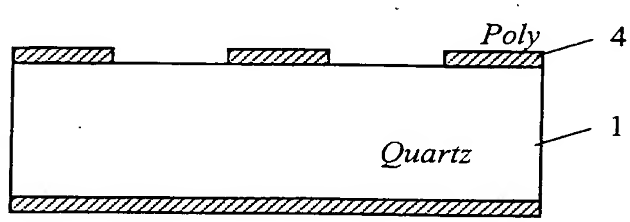


Fig. 8F

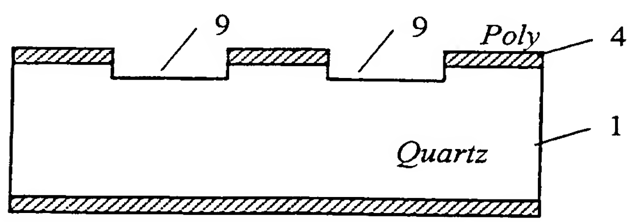


Fig. 8G

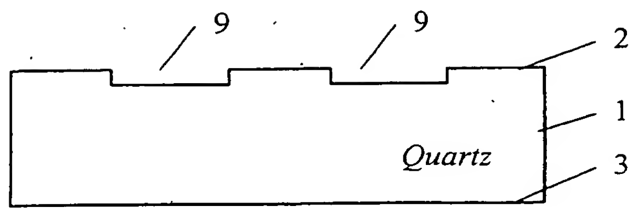


Fig. 8H

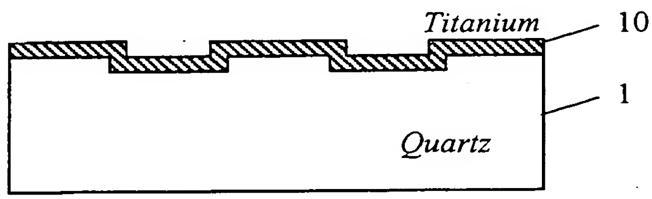


Fig. 8I

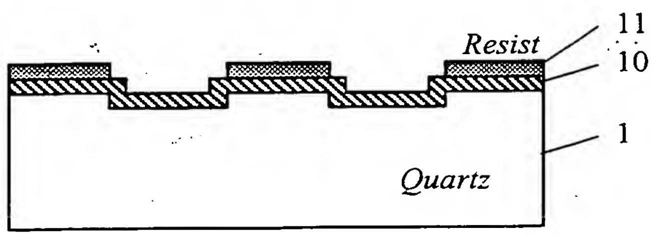


Fig. 8J

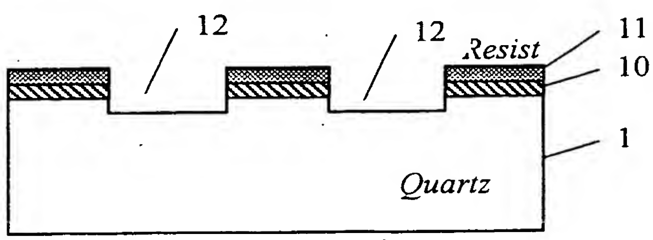


Fig. 8K

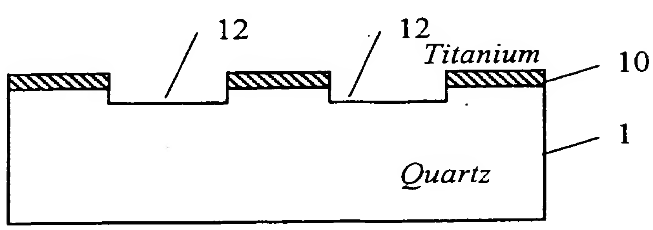


Fig. 8L

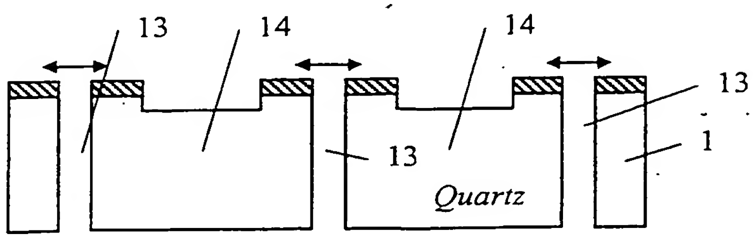


Fig. 8M

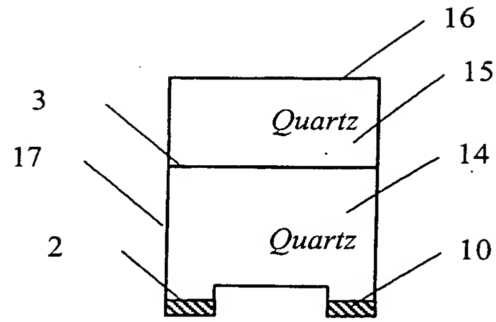


Fig. 8N

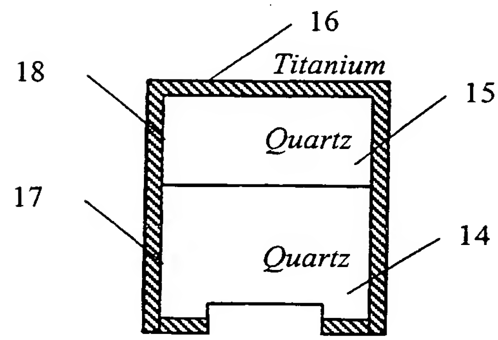


Fig. 8O

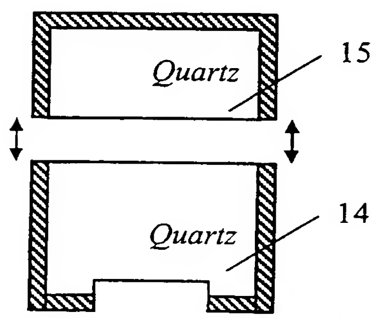
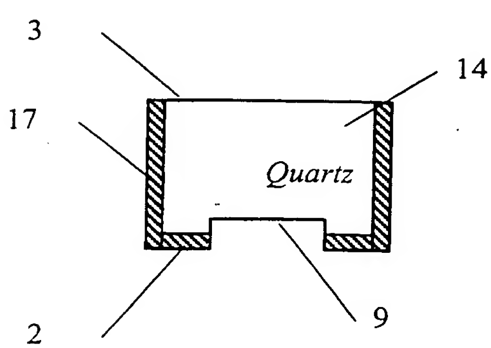


Fig. 8P



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 June 2001 (21.06.2001)

PCT

(10) International Publication Number
WO 01/44875 A3

(51) International Patent Classification[7]: G03F 7/00, 7/20, B29C 35/00

(21) International Application Number: PCT/US00/41781

(22) International Filing Date: 31 October 2000 (31.10.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
09/464,380 15 December 1999 (15.12.1999) US

(71) Applicant: NANOGEN, INC. [US/US]; 10398 Pacific Center Drive, San Diego, CA 92121 (US).

(72) Inventors: EVANS, John; 14055 Tahiti Way, Marina del Ray, CA 90292 (US). HAVENS, John, R.; 5628 Lamas Street, San Diego, CA 92122 (US). HARVEY, Noel; 3211 US 70 West, Efland, NC 27243 (US). SMOLKO, Dan; 20555 Bee Valley Road, Jamul, CA 91935 (US).

(74) Agents: EAGLEMAN, Patrick, S. et al.; Lyon & Lyon LLP, 633 West Fifth Street, Suite 4700, Los Angeles, CA 90071-2066 (US).

(81) Designated States (*national*): AU, BR, CA, CN, JP, KR, NZ.

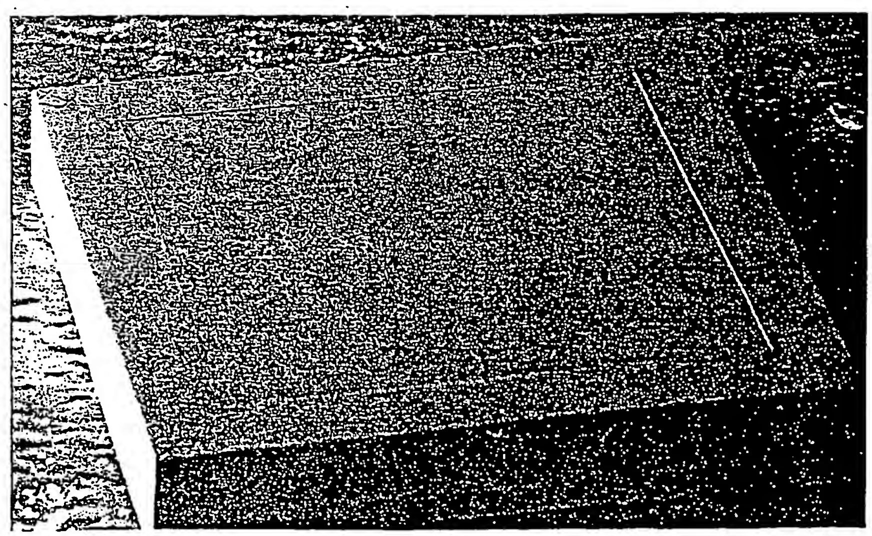
(84) Designated States (*regional*): European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published:
— *with international search report*

(88) Date of publication of the international search report: 27 June 2002

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MICROMOLDS FABRICATED USING MEMS TECHNOLOGY AND METHODS OF USE THEREFOR



(57) Abstract: A method of making microreaction molds for grafting and molding very thin films onto surfaces of materials such as microchips is provided. The methods utilize MEMS technology to achieve the manufacture of molds that have a high degree of consistency and uniformity in the thicknesses of the films applied to the surfaces. Use of MEMS technology allows such molds to be made with an accuracy of less than 1 µm in mold depth. The method provides for the manufacture of molds from a single transparent material that is able to be etched in a consistent manner. The method of this invention is particularly applicable to mass generation of microchip surfaces having uniform thin polymeric films bound thereto.

WO 01/44875 A3

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 00/41781

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/00 G03F7/20 B29C35/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G03F B29C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 259 926 A (KUWABARA KAZUHIRO ET AL) 9 November 1993 (1993-11-09) the whole document ---	1-34
X	HAISMA J ET AL: "MOLD-ASSISTED NANOLITHOGRAPHY: A PROCESS FOR RELIABLE PATTERN REPLICATION" JOURNAL OF VACUUM SCIENCE AND TECHNOLOGY: PART B, AMERICAN INSTITUTE OF PHYSICS. NEW YORK, US, vol. 14, no. 6, 1 November 1996 (1996-11-01), pages 4124-4128, XP000721137 ISSN: 0734-211X the whole document --- -/--	1-3, 7-20, 24-34

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed
- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 August 2001	22/08/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Haenisch, U

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 623 440 A (KONINKL PHILIPS ELECTRONICS NV) 9 November 1994 (1994-11-09) the whole document	1-3, 7-20, 24-34
X	US 4 543 225 A (BEAUJEAN JOSEPH M E) 24 September 1985 (1985-09-24) the whole document	1-34
A	US 5 171 392 A (IIDA TETSUYA ET AL) 15 December 1992 (1992-12-15)	
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 207 (P-1207), 28 May 1991 (1991-05-28) & JP 03 054569 A (DAINIPPON PRINTING CO LTD), 8 March 1991 (1991-03-08) abstract	
A	EP 0 156 372 A (HITACHI LTD ;HITACHI MAXELL (JP)) 2 October 1985 (1985-10-02)	

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 00/41781

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5259926	A	09-11-1993	JP	5080530	A	02-04-1993
EP 0623440	A	09-11-1994	DE	69405451	D	16-10-1997
			DE	69405451	T	12-03-1998
			JP	7005693	A	10-01-1995
			US	5425848	A	20-06-1995
US 4543225	A	24-09-1985	EP	0168530	A	22-01-1986
			AT	51577	T	15-04-1990
			DE	3481831	D	10-05-1990
US 5171392	A	15-12-1992	JP	2223030	A	05-09-1990
			JP	8023941	B	06-03-1996
			DE	68922185	D	18-05-1995
			DE	68922185	T	09-11-1995
			EP	0368442	A	16-05-1990
			US	5126996	A	30-06-1992
JP 03054569	A	08-03-1991	NONE			
EP 0156372	A	02-10-1985	JP	60202557	A	14-10-1985